19 JAN 2005

Europäische **Patentamt** 

European **Patent Office**  Office ( péen des bre

14.00003

REC'D 29 AUG 2003

WIPO PCT

Bescheinigung

Certificate

**Attestation** 

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application conformes à la version described on the following page, as originally filed.

Les documents fixés à cette attestation sont initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patent application No. Demande de brevet no Patentanmeldung Nr.

02016085.9



Der Präsident des Europäischen Patentamts; Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets p.o.

R C van Dijk



European Patent Office Office européen des brevets



Anmeldung Nr:

Application no.:

02016085.9

Demande no:

Anmeldetag:

Date of filing: 19.07.02

Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. Carel van Bylandtlaan 30 2596 HR Den Haag PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention: (Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung. If no title is shown please refer to the description. Si aucun titre n'est indiqué se referer à la description.)

Use of condensing boiler

In Anspruch genommene Prioriät(en) / Priority(ies) claimed /Priorité(s) revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/Classification internationale des brevets:

F24H/

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

- 1 -

TS 8578 EPC

#### USE OF A CONDENSING BOILER

The invention is directed to an improved use of a condensing boiler. This invention relates to boilers and, in particular, to condensing boilers typically used for heating water for commercial or domestic applications such as space heating and domestic water heating.

5

10

15

20

25

Condensing boilers are described in EP-A-0789203. This publication describes a gas fired condensing boiler. These boilers are called condensing boilers because the gases produced by combustion are cooled inside the apparatus until the water vapour contained therein condenses, so as to recover the latent condensation heat and transfer it to the water to be heated, which flows through said boilers. This latent heat is sometimes also used to pre-heat the combustion air. A problem associated with these condensing boilers is that the liquid condensate by-products of the combustion must be contained and channelled away for disposal. Furthermore heat exchanger materials must be capable of withstanding the corrosive liquid condensate by-products. Steps should also be taken to ensure that the burner and igniter systems, along with other system elements such as sensors, are not fouled by moisture or condensation.

Normally condensing boilers use natural gas as fuel. For example in The Netherlands, which is equipped with a wide spread natural gas grid, many households use a condensing boiler for domestic heating in combination with warm water supply. The wide application of these condensing boilers is due to the attractive energy

efficiency of these apparatuses and the presence of the natural gas supply grid.

5

10

15

20

25

30

A disadvantage of these apparatuses is that they cannot be easily applied in regions where no natural gas grid is present. A solution to this problem is to use a liquid fuel. Liquid fuels can be easily transported to and stored by the end user. A disadvantage of the use of liquid fuels is however that the condensing boiler and/or the associated chimneys have to be made from different, more corrosion resistance, materials. This is a disadvantage for the manufacturer of condensing boilers because it would result in two types of boiler apparatuses. Moreover the apparatus using a liquid fuel would be more expensive due to the different more corrosive-resistant material required.

The object of the present invention is to provide a condensing boiler solution for regions not equipped with a natural gas supply grid.

This object is achieved by the following use. Use of a Fischer-Tropsch derived fuel in a condensing boiler.

Applicants have found that the corrosive nature of the condensate liquid by-product as produced when a Fischer-Tropsch derived fuel is used is low. The corrosive nature of the condensate liquid by-product is lower when compared to the condensate liquid by-product as obtained when an (low-sulphur) industrial gas oil (IGO) is used as fuel. The corrosive nature is such that a condensing boiler suitable for gas firing can also be used for liquid fuel firing. Some small adjustments to the burner may be necessary. This is however much less cumbersome as to apply different materials for, for example, the heat exchanging surfaces of the condensing boiler and/or the chimney.

Furthermore less NOx emissions have been found when emissions of a Fischer-Tropsch derived fuel are compared to those of an Industrial Gas Oil. A next advantage is that less odor, less hydrocarbon emissions and less carbon monoxide emissions during start and extinction of the burner have been observed when using this fuel. This is very advantageous because the burner of a condensing boiler will very often start and stop.

5

10

15

20

25

30

A next advantage is that Fischer-Tropsch derived fuels are very stable and can be stored for a prolonged period of time. This is advantageous when such a fuel is stored for domestic use. In spite of its stability the Fischer-Tropsch derived fuel is also biodegradable making it a very environmental friendly fuel.

Figure 1 shows a schematic representation of such a condensing boiler.

Figure 1 shows a wall-mounted condensing boiler housing 1 comprising a centrally positioned burner 2. The burner flame exists in a combustion space 3, which is confined by an end wall 4 and a heat exchanger tube wall 5. Flue gasses can leave the combustion space 3 through openings in the wall 5 to enter an annular space 6, which is confined by further heat exchanger tube wall segments 7. The housing 1 further is provided with means 14 to supply cold water to the heat exchanger tube wall 4,5 and means 15 to discharge heated water from said tube wall 4,5. The housing 1 is further provided with a chimney 8 for discharging flue gas fluidly connected to space 6. The air provided to burner 2 via van 16 is preheated against flue gas leaving the housing by passing the air counter currently along the chimney 8 in an annular space 9. In the chimney 9 water condensates and the condensate is discharged to a drain 10 via

conduit 11. An oil pump 12 to supply the Fischer-Tropsch fuel and an expansion vessel 13 is also shown in Figure 1.

The burner used in the condensing boiler may be a yellow flame burner or preferably a blue flame burner. Yellow and blue flame burners are well known types of burners and are for example described in the general textbook, "Heizung + Klimatechnik 01/02" German Version by Recknagel, Sprenger, Schramek, ISBN: 3-468-26450-8, on pages 718-719.

5

10

15

20

25

30

Yellow flame burners are often provided with a flame detector. Most detectors, which are used today, detect a particular wavelength associated with the yellow colour of the flame. Applicants have now found that when a Fischer-Tropsch derived fuel is used the commonly known detectors fail to observe the resulting blue coloured flame. For this reason the yellow flame burner is preferably provided with a detector, which can detect this blue flame. Examples of suitable detectors are the detectors that are used in blue flame burners. Alternatively additives may be added to the Fischer-Tropsch derived fuel which result in a flame which can be detected by the above standard yellow flame burner detector.

The operating conditions of the yellow or blue flame burner may be the same as the operating conditions used for the state of the art liquid fuels. The proportion of air in excess of that required for stoichiometric combustion is known as the excess air ratio or "lambda", which is defined as the ratio of total air available for combustion to that required to burn all of the fuel. Preferably the lambda is between 1 and 2 and more preferably between 1 and 1.6. Applicants found that by

using a Fischer-Tropsch derived fuel a very low lambda of between 1.05 and 1.2 could be applied without large emissions of carbon monoxide, as would be the case when Industrial Gas Oil would be used.

5

10

15

20

25

30

The Fischer-Tropsch derived fuel will comprise a Fischer-Tropsch product which may be any fraction of the middle distillate fuel range, which can be isolated from the (hydrocracked) Fischer-Tropsch synthesis product. Typical fractions will boil in the naphtha, kerosene or gas oil range. Preferably a Fischer-Tropsch product boiling in the kerosene or gas oil range is used because these fractions are easier to handle in for example domestic environments. Such products will suitably comprise a fraction larger than 90 wt% which boils between 160 and 400 °C, preferably to about 370 °C. Examples of Fischer-Tropsch derived kerosene and gas oils are described in EP-A-583836, WO-A-9714768, WO-A-9714769, WO-A-011116, WO-A-011117, WO-A-0183406, WO-A-0183648, WO-A-0183647, WO-A-0183641, WO-A-0020535, WO-A-0020534, EP-A-1101813, US-A-5766274, US-A-5378348, US-A-5888376 and US-A-6204426.

The Fischer-Tropsch derived product will suitably contain more than 80 wt% iso and normal paraffins and less than 1 wt% aromatics, the balance being naphthenics compounds. The content of sulphur and nitrogen will be very low and normally below the detection limits for such compounds. This low content of these elements is due to the specific process wherein the Fischer-Tropsch reaction is performed. The content of sulphur will therefore be below 5 ppm and the content of nitrogen will be below 1 ppm. As a result of the low contents of aromatics and naphthenics compounds the density of the Fischer-Tropsch product will be lower than the conventional mineral

derived fuels. The density will be between 0.65 and 0.8  $g/cm^3$  at 15 °C.

The fuel used in the process of the present invention may also comprise fuel fractions other than the Fischer-Tropsch product. Examples of such fractions may be the kerosene or gas oil fractions as obtained in traditional refinery processes, which upgrade crude petroleum feedstock to useful products. Preferred non-Fischer-Tropsch fuel fractions are the ultra low sulphur (e.g. less than 50 ppm sulphur) kerosene or diesel fractions, which are currently on the market. Optionally non-mineral oil based fuels, such as bio-fuels, may also be present in the fuel composition. The content of the Fischer-Tropsch product component in the fuel will be preferably be above 40 wt%, more preferably above 60 wt% and most preferably above 80 wt%. It should be understood that the content of such, currently less available, Fischer-Tropsch product will be optimised, wherein pricing of the total fuel will be balanced with the advantages of the present invention. For some applications fuels fully based on a Fischer-Tropsch product plus optionally some additives may be advantageously used.

10

15

20

25

30

The fuel may also comprise one or more of the following additives. Detergents, for example OMA 350 as obtained from Octel OY; stabilizers, for example Keropon ES 3500 as obtained from BASF Aktiengesellschaft, FOA 528A as obtained from OCTEL OY; metal-deactivators, for example IRGAMET 30 (as obtained from Specialty Chemicals Inc; (ashless) dispersants, for example as included in the FOA 528 A package as obtained from Octel OY; anti-oxidants: IRGANOX LO6, or IRGANOX L57 as obtained from Specialty Chemicals Inc; cold flow improvers, for example Keroflux 3283 as obtained from

BASF Aktiengesellschaft, R433 or R474 as obtained from Infineum UK Ltd; combustion improver, for example ferrocene, methylcyclopentadienylmanganese-tricarbonyl. (MMT); anti-corrosion: Additin RC 4801 as obtained from Rhein Chemie GmbH, Kerocorr 3232 as obtained from BASF, SARKOSYL 0 as obtained from Ciba; re-odorants, fro example Compensol as obtained from Haarmann & Reimer; biociodes, for example GROTA MAR 71 as obtained from Schuelke & Mayr; lubricity enhancers, for example OLI 9000 as obtained from Octel; dehazers, for example T-9318 from Petrolite; antistatic agents, for example Stadis 450 from Octel; and foam reducers, for example TEGO 2079 from Goldschmidt.

The total content of the additives may be suitably between 0 and 1 wt% and preferably below 0.5 wt%.

The invention will now be illustrated with the following non-limiting examples.

#### Example 1

5

10

15

20

25

To a blue flame burner type BNR 10 (Intercal Wearmetechnik GmbH) as placed in a Therma Nova 2025 condensing boiler (Therma Tec GmbH) a Fischer-Tropsch gas oil (Oil A), an ultra low sulphur gas oil (Oil B) and a standard industrial gas oil (Oil C) having the properties as listed in Table 1 was fed at a constant power level. The oils contained the same standard additive package. The condensing boiler type was operated such that condensation of water as present in the flue gas took place on both the heat exchanging surfaces of the boiler as well as in the chimney.

Table 1

	T=: ;		
	Fischer-	Reference	Reference
	Tropsch	oil-1 (B)	oil-2 (C)
1.	gas oil		·
	(A)	·	·
Density	785.2	854.3	846.3
(at 15 ℃			
in kg/m <sup>3</sup>		·	
Sulphur	< 0.0001	0.142	0.061
content			
(wt%)			
Kinematic	6.444	3.842	4.621
viscosity			·
at 20 °C			
(mm <sup>2</sup> /s)	•		
Flash	92	. 64	66 ·
point (°C)			,

The condensate liquid was collected with a drain and the iron and nickel content was measured. The results are presented in Table 2. The higher the iron and nickel content the higher the rate of corrosion in the condensing boiler. The results in Table 2 clearly show that when a Fischer-Tropsch fuel is used considerably less corrosion occurs.

5

Table 2

	Iron content in	Nickel content in	
	condensate (mg/kg)	condensate (mg/kg)	
Fischer-	0.06	0.01	
Tropsch fuel			
IGO	1.85	0.06	
IGO low	1.03	0.06	
sulphur			

TS 8578 EPC

#### CLAIMS

- 1. Use of a Fischer-Tropsch derived fuel in condensing boiler.
- 2. Use according to any one of claims 1-5, wherein the Fischer-Tropsch derived fuel boils for more than 90 wt% between 160 and 400 °C.

5

20.

- 3. Use according to claim 6, wherein the Fischer-Tropsch derived fuel boils for more than 90 wt% between 160 and 370 °C.
- 4. Use according to any one of claims 1-7, wherein the Fischer-Tropsch derived fuel comprises a Fischer-Tropsch product which contains more than 80 wt% of iso and normal paraffins, less than 1 wt% aromatics, less than 5 ppm sulphur and less than 1 ppm nitrogen and wherein the density of the Fischer-Tropsch product is between 0.65 and 0.8 g/cm<sup>3</sup> at 15 °C.
  - 5. Use according to any one of claims 1-8, wherein the Fischer-Tropsch derived fuel comprises more than 80 wt% of a Fischer-Tropsch product.
  - 6. Use according to claim 9, wherein the Fischer-Tropsch derived fuel comprises a mineral oil fraction and/or a non-mineral oil fraction.
    - 7. Use according to any one of claims 1-6, wherein the burner of the condensing boiler is a yellow flame or a blue flame burner.
- 8. Use according to claim 7, wherein the lambda is between 1 and 1.6
  - 9. Use according to claim 8, wherein the lambda is between 1.05 and 1.2.

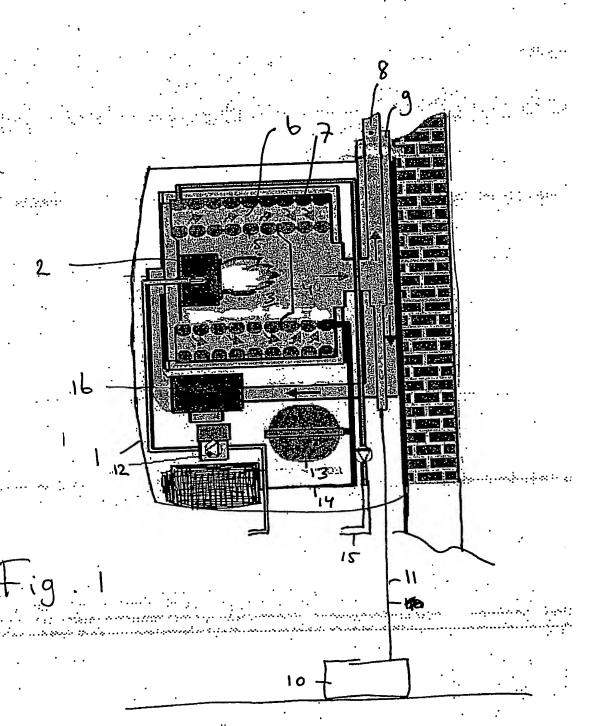
10. Use according to any one of claims 7-9, wherein more than 3 starts per hour are made with the yellow or blue flame burner.

TS 8578 EPC

#### ABSTRACT

USE OF A CONDENSING BOILER

Use of a Fischer-Tropsch derived fuel in condensing boiler. The fuel comprises a Fischer-Tropsch product which boils for more than 90 wt% between 160 and 400 °C and contains more than 80 wt% of iso and normal paraffins, less than 1 wt% aromatics, less than 5 ppm sulphur and less than 1 ppm nitrogen and wherein the density of the Fischer-Tropsch product is between 0.65 and 0.8 g/cm<sup>3</sup> at 15 °C.



# This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

### **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

□ BLACK BORDERS
□ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
□ FADED TEXT OR DRAWING
□ BLURRED OR ILLEGIBLE TEXT OR DRAWING
□ SKEWED/SLANTED IMAGES
□ COLOR OR BLACK AND WHITE PHOTOGRAPHS
□ GRAY SCALE DOCUMENTS
□ LINES OR MARKS ON ORIGINAL DOCUMENT
□ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

## IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

OTHER: